

Local Tunneling Study of Three-Dimensional Order Parameter in the π -band of Al-doped MgB_2 Single Crystals

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We have performed local tunneling spectroscopy on high quality $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ single crystals by means of Variable Temperature Scanning Tunneling Spectroscopy (STS) in magnetic field up to 3 Tesla. Single gap conductance spectra due to c -axis tunneling were extensively measured, probing different amplitudes of the three-dimensional Δ_π as a function of Al content. Temperature and magnetic field dependences of the conductance spectra were studied in S-I-N configuration: the effect of the doping resulted in a monotonous reduction of the locally measured T_C down to 24K for $x=0.2$. On the other hand, we have found that the gap amplitude shows a maximum value $\Delta_\pi = 2.3$ meV for $x=0.1$, while the Δ_π/T_C ratio increases monotonously with doping. The locally measured upper critical field was found to be strongly related to the gap amplitude, showing the maximum value $H_{c2} \simeq 3T$ for $x=0.1$ substituted samples. For this Al concentration the data revealed some spatial inhomogeneity in the distribution of Δ_π on nanometer scale.

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Five years after Nagamatsu et al. [1] reported MgB_2 to be superconductor, the huge worldwide experimental and theoretical effort seems to have established the main features of superconductivity in this compound. Indeed, the strong electronic coupling to the high-frequency in-plane boron modes (E_{2g} at the zone centre Γ) and the number of holes at the Fermi level in the σ bands are able to explain a transition temperature T_C as high as 39 K [2, 3]. Moreover, it is now demonstrated [4, 5, 6, 7, 8, 9, 10, 11, 12] that MgB_2 is a two-gap superconductor with two distinct energy gaps: a large gap Δ_σ originating from two-dimensional (2D) σ bands and a small gap Δ_π originating from three-dimensional (3D) π bands. The presence of two bands with distinct superconducting gaps leads to several unusual properties, like the temperature and field dependent anisotropy which dominate the magnetic and transport properties. Anisotropy is related to the intraband and interband electron scattering that can be modified by partial chemical substitutions. In particular, aluminium (replacing magnesium) [13], and carbon (replacing boron) [14] have successfully entered in the MgB_2 structure, doping the material with additional electrons: small variations of the interband scattering have been predicted for C substitutions, while it has been demonstrated that Al doping can realize a considerable out-of-plane distortions of the B atoms [15] causing a significant increase of the interband scattering with consequent increasing of Δ_π and decreasing of Δ_σ [16].

Experimentally, it has been observed that the superconducting transition temperature of both $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ and $\text{Mg}(\text{B}_{1-y}\text{C}_y)_2$ decreases with doping [13, 17] and

in the case of Al (C), superconductivity disappears for $x > 0.5$ ($y > 0.3$) [18, 19]. Recently, measurements of the amplitude of the energy gaps have been performed by means of different techniques (specific heat, point contact, STM) on Al doped [20, 21] as well as on neutron irradiated polycrystals [22, 23] and on disordered thin films [24]. From these studies a quite general trend seems to relate the variation of both energy gaps with T_C , however a different behavior of Δ_π has been reported for Al-doped single-crystals, indicating large gap values for doping levels up to 10% and quite small values for higher doping levels [25, 26]. Results on C-doped samples also are controversial and the analysis of the whole set of data resulted in an extended debate [27, 28, 29] still waiting for a definite answer. It is our opinion that in some cases, disagreement arises due to the non-local nature of used experimental techniques and to the high number of fitting parameters necessary to reproduce the experiments.

In this paper we report a systematic study performed by Scanning Tunneling Spectroscopy (STS) on high quality $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ single crystals, for different Al concentrations. Directional tunneling along c -axis allowed us to selectively probe the π band energy gap, with high spatial and energy resolution. In particular, by measuring the temperature dependence of the tunneling spectra, the local T_C was inferred, corresponding to the energy gap measured in the same location. The magnetic field dependence was also studied to evidence correlations of the locally measured upper critical field H_{c2} with the gap amplitude. Moreover, the high spatial resolution of the STS technique allowed to evidence possible non-homogeneities of the superconducting properties on the sample surface

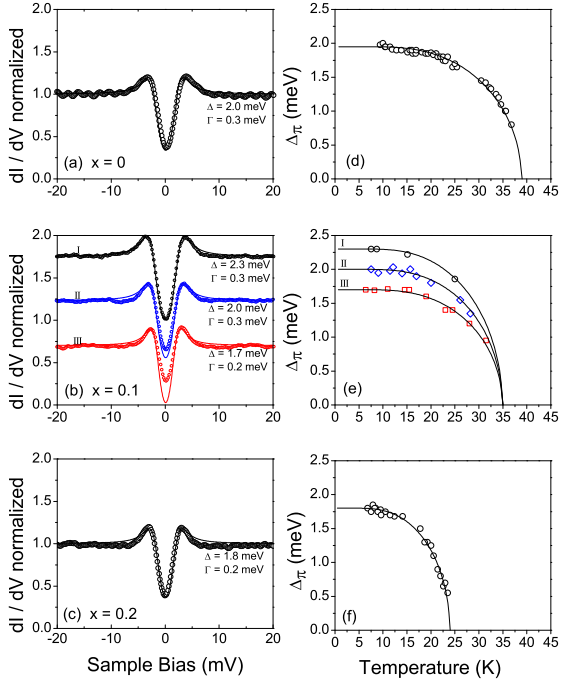


FIG. 1: Left plots: Low temperature spectra measured in $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ for $x = 0$ (a), $x=0.1$ (b) and $x=0.2$ (c). Solid lines represent the theoretical fittings calculated by considering a single gap isotropic BCS density of states with a smearing Γ parameter. Right plots: corresponding temperature dependence of the superconducting energy gap Δ_π as extracted from the theoretical fittings. Experimental data are compared to the theoretical BCS behavior (solid lines).

with variation of Δ_π depending on the doping.

Single crystals of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ were grown by high pressure method in a cubic-anvil press in the same way as the pure crystals [30]. The STS experiments were carried out on crystals with nominal 0%, 10% and 20% Al content by means of an UHV variable temperature STM. The tunneling junctions were achieved by approaching a mechanically etched Pt/Ir tip to the c -axis oriented surface of the crystals. As expected, the STS measurements revealed only a single gap structure in the dI/dV spectra at low temperatures because the probability for direct tunneling into the 3D-sheet of the Fermi surface results much higher than the probability for tunneling into the 2D-part of the Fermi surface which has no states with wavevector parallel to the c -axis.

In Fig. 1a,b,c we show the dI/dV characteristics measured at $T = 6.5$ K respectively on pure MgB_2 , and on samples with 10% ($x=0.1$) and 20% ($x=0.2$) Al content. It can be observed that all the tunneling spectra are well reproduced by an isotropic BCS state density with a single gap value Δ_π , corresponding to the 3D π -band, and a phenomenological smearing factor Γ , corresponding to finite lifetime of the quasiparticles, as introduced by Dynes [31]. These are the only two fitting parameters needed to model the experimental data while the temperature

was directly measured. The experiments indicated that pure MgB_2 crystals were highly homogeneous with the sample surface characterized by a superconducting energy gap $\Delta_\pi = 2.00 \pm 0.05$ meV, i.e. with less than 3% spread in the values measured in different locations.

The behavior of the doped crystals appeared to be quite different. For the $x=0.1$ substituted crystals, the 3D Δ_π resulted to be non-homogeneous in its spatial distribution on nanometer scale, with values varying between $1.5 \text{ meV} < \Delta_\pi < 2.3 \text{ meV}$, as observed in Fig. 1b referring to different locations of the same sample. The spectrum signed (I) for which we found $\Delta_\pi = 2.3$ meV, was the statistically most present in about 90% of the locations. However, in few cases, we have measured different gap amplitudes as observed in curve (II) with $\Delta_\pi = 2.0$ meV and in curve (III) with $\Delta_\pi = 1.7$ meV. The energy gap variations in the $x=0.1$ substituted samples, can be due to different local Al concentrations arising during the crystal growth process. Indeed, structural changes can occur in crystals when the Al content is increased beyond a critical value $x \simeq 0.1$. These changes include the segregation of a non-superconducting, Al-rich phase and the formation of superstructures along the c -axis [26]. We notice that the most satisfactory agreement between theory and experiments was obtained for the spectra statistically more present characterized by the largest value of the energy gap, $\Delta_\pi = 2.3$ meV, corresponding to a 15% increase of the superconducting energy gap compared to the case of pure MgB_2 . For the $x=0.2$ substituted crystals, statistic in several locations showed quite homogeneous superconducting properties on the sample surface. The measured spectra evidenced single gap features (Fig. 1c) with $\Delta_\pi = 1.8$ meV, with less than 6% spread in the measured values. We notice that this last estimation results much higher than what previously reported for similar doping levels [25].

For all samples, we have performed complete measurements of the temperature dependence of the tunneling spectra in the range between 5 K and 40 K. In Fig. 1d,e,f, the gap amplitude as inferred from the theoretical fittings is plotted as a function of the temperature. In the case of pure MgB_2 (Fig. 1d), a BCS dependence (solid line) of the data (scattered symbols) is found indicating a local $T_C = 39$ K. In the case of 10% Al-doping (Fig. 1e), gaps of different amplitudes all vanish at the same critical temperature $T_C \simeq 35$ K indicating that variations of the 3D order parameter in the π -band occur on a scale less than the superconducting coherence length. For samples with higher doping level, $x=0.2$ (Fig. 1f), a local $T_C = 24$ K is found.

We also performed a complete analysis of the local response to external magnetic fields up to 3 T, with the tunneling current and the applied field parallel to the c -axis of the crystal. The samples were cooled in zero magnetic field. At low temperature, the field was slowly increased from zero up to 3 T and then reduced to zero again, to evidence any hysteretic behavior. Since the reported spectra were averaged over many vortices passing

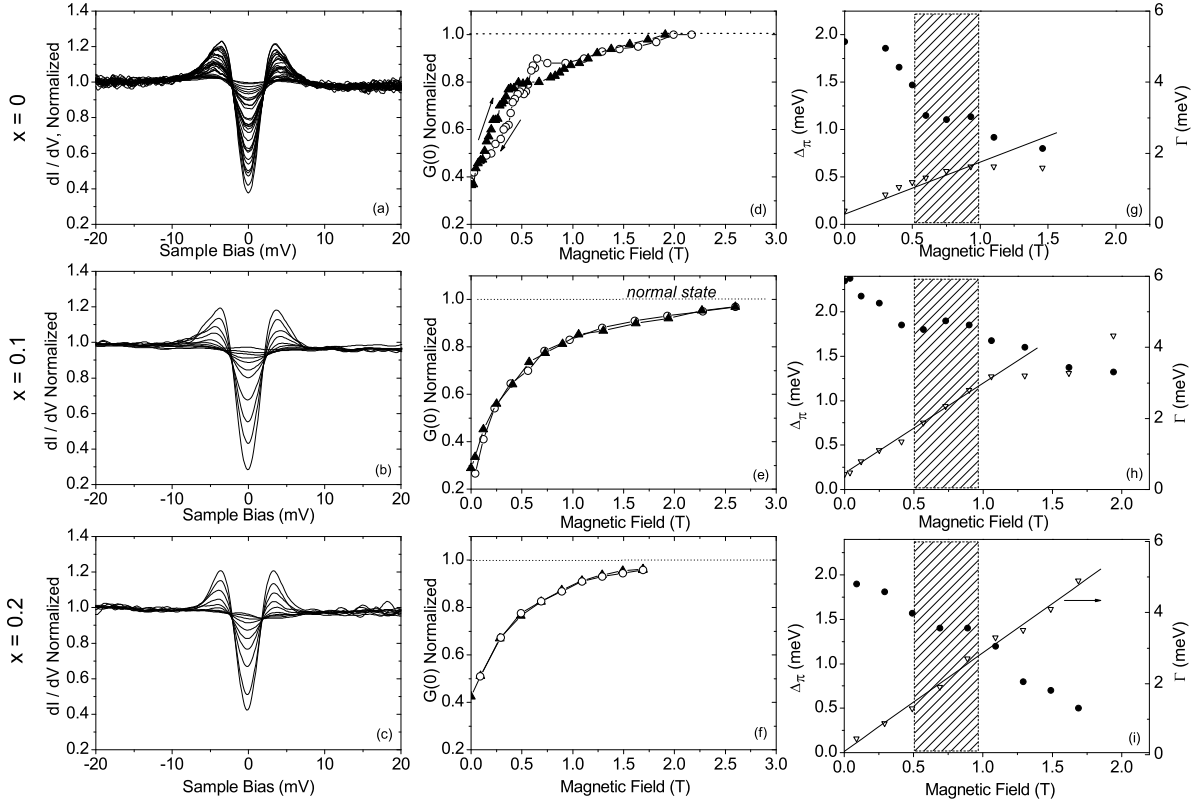


FIG. 2: Magnetic field dependence of the conductance spectra measured at $T \simeq 6.5K$. Different doping levels are reported on different rows. In the first column the tunneling conductance spectra measured for rising fields are reported. In the central column the field evolution of the ZBC, for increasing (solid triangles) and decreasing (empty circles) fields, are shown. In the third column the magnetic field dependence of the 3D Δ_π as obtained by theoretical fitting is presented. Solid symbols refer to the energy gap amplitude, while open symbols refer to the Γ values.

under the tip [32], the main effect of the magnetic field was, as expected, the progressive filling of states inside the energy gap.

In Fig. 2 we show a complete set of data recorded in magnetic field for $x=0$ (Fig. 3a,d,g), $x=0.1$ (Fig. 2b,e,h), and $x=0.2$ (Fig. 2c,f,i). In the first column we show the evolution of the normalized tunneling conductance spectra as measured at $T \simeq 6.5K$. The field dynamics of the DOS at the Fermi level is reported in the second column where the evolution of the Zero-Bias Conductance (ZBC) is presented. We notice that for pure crystals (Fig. 2d), the ZBC rapidly rises for low fields and reaches a value of about 80% of the normal state ZBC around 0.4 T. As the field further increases, the filling of states becomes much slower, the two different dynamics being separated by an almost flat crossover region. Finally, the gap fills completely around 2.2 T. By lowering the field we observed a similar behavior, with the crossover region slightly shifted to higher fields. We speculate that the crossover region can be associated to the rotation of the vortex lattice in the pure MgB_2 [33], while the hysteretic behavior seems to indicate different vortex dynamics for increasing and decreasing fields, which may be due to geometrical barriers, vortex pinning, and/or lattice re-arrangements.

In the case of 10% Al doping (Fig. 2e), the data refer to locations with $\Delta_\pi = 2.3$ meV. The field dynamics of the DOS at the Fermi level again shows a rapid rising of the ZBC for low magnetic fields. However, for increasing fields, the filling of states tends to saturate and, at 2.5 T, it is still possible to distinguish the presence of the superconducting energy gap in the measured spectra. Extrapolation of the data in this region leads to $H_{c2} \simeq 3$ T, corresponding to a value 30% higher than that observed in the case of pure MgB_2 . For $x=0.2$, the ZBC evolution in magnetic field indicates a reduced $H_{c2} \simeq 1.8$ T. We notice that, for both substitutions, the ZBC doesn't show any hysteretic behavior. Finally, in Fig. 2c,f,i we show the magnetic field dependence of Δ_π for the three samples as inferred from the theoretical fittings. We observe a clear reduction of the gap amplitude for fields up to 0.5 T followed by a region between 0.5 T and 1.0 T, in which no significant variations occur, while pair-breaking continuously increases due to the applied magnetic field. This observation seems to suggest that around 0.5 T the contribution to the superconductivity due to the phonon mediated electron-electron interactions in the π -band itself is not efficient anymore, while for higher fields the energy gap survives due to both the phonon exchange

TABLE I: Summary of our STM results.

x	T_C (K)	Δ_π (meV)	H_{c2} (T)	$2\Delta_\pi/K_B T_C$
0	39	2.0	2.2	1.17
0.1	35	2.3	3.0	1.52
0.2	24	1.8	1.8	1.74

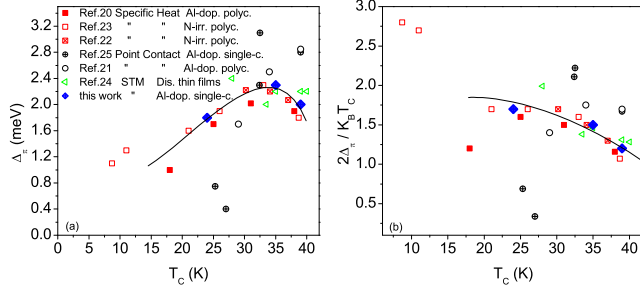


FIG. 3: (a) $\Delta_\pi(0)$ and (b) $2\Delta_\pi(0)/K_B T_C$ as function of T_C , compared with data in literature. Same symbols have been used in both plots and the full lines are guides to the eye.

with σ -band [34] and/or to the quasiparticle interband scattering.

Finally, in Table I we summarize our results that in Fig. 3 are compared with the literature. The significant spread of the data reported by different groups is at the origin of the recent, hot debate [27, 28, 29], nevertheless a quite general trend (full lines) for both the

3D energy gap $\Delta_\pi(0)$ and the $2\Delta_\pi(0)/K_B T_C$ ratio as a function of T_C can be inferred regardless to the nature of the measured samples: doped/irradiated/disordered - single crystals/polycrystals/thin films. The monotonous increase of the $2\Delta_\pi(0)/K_B T_C$ ratio and the maximum value of $\Delta_\pi(0)$ found for $x=0.1$ appear as a strong confirmation of the hypothesis due to A. Bussmann-Holder and A. Bianconi [16] with our data adding a clear relation between the locally measured values of $\Delta_\pi(0)$ and H_{c2} .

In conclusion, we have performed a systematic study of the local temperature and magnetic field dependence of the 3D energy gap Δ_π in $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ single crystals by means of Scanning Tunneling Spectroscopy. By working with high quality single crystals we succeeded to selectively measure the behavior of the only Δ_π , and due to the high spatial resolution of the STS technique, we were able to relate the local values of T_C , Δ_π and H_{c2} . We have found a reduction of T_C for increasing doping, corresponding to a monotonous rising of the BCS ratio but not of the absolute amplitude of the energy gap. In agreement with recent theoretical models, we have measured the largest gap value ($\Delta_\pi = 2.3$ meV, 15% larger than in pure MgB_2) in samples with $x=0.1$, corresponding to a local $H_{c2}^{\parallel c} \simeq 3\text{T}$ (30% higher than in pure MgB_2).

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